

The effect of polydispersity on measuring polymer self-diffusion with the n.m.r. pulsed field gradient technique

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(Received 17 January 1985; revised 27 March 1985)

The echo attenuation in the n.m.r. pulsed field gradient technique for polydisperse samples ($\bar{M}_w/\bar{M}_n = 1.06, 2.0$ and 10) was calculated, which, for the smallest polydispersity, is already markedly nonexponential. The echo attenuations of solutions of a polydisperse polystyrene, mixtures of monodisperse polystyrenes and the melt of a commercial polyethylene were measured. In the solutions, depending on the concentration regime, the echo attenuations were considerably less nonexponential than calculated and often exponential within experimental error giving one averaged self-diffusion coefficient. An averaging of the self-diffusion process does exist which is not in accordance with the reptation concept. In the entangled melt the echo attenuation is the sum of the contributions of the different molar masses, where no averaging is present, but, due to the strong dependence of the nuclear relaxation times on molar mass, the smaller molar masses are more strongly weighted and a dependence of the echo attenuation on the diffusion time arises.

(Keywords: polydispersity; self-diffusion; nuclear magnetic resonance pulsed field gradient technique; solutions; melts)

INTRODUCTION

A large part of polymer self-diffusion studies in solution and in the melt is performed using the n.m.r. pulsed field gradient technique (see e.g. ref. 1). The essential dependence of the self-diffusion coefficient of macromolecules on concentration and molar mass for solutions and the melt are now well documented²⁻⁶. An important problem in measuring self-diffusion coefficients with the n.m.r. pulsed field gradient technique, however, is the effect of the polydispersity of the samples. In a paper by von Meerwall⁷ the interpretation of n.m.r. pulsed field gradient technique experiments with polydisperse samples is discussed for dilute polymer solutions. From a more general point of view Bernard and Noolandi investigated the influence of polydispersity on self-diffusion measurements with special attention to forced Rayleigh scattering experiments⁸, and Callaghan and Pinder discussed some aspects of this problem in an investigation of polydisperse dextrans in water⁹. However, in most experimental investigations of polymer self-diffusion using the n.m.r. pulsed field gradient technique, the polydispersity of the samples has received little attention.

Clearly this problem could be ignored by most authors although the self-diffusion coefficient of polymer molecules strongly depends on molar mass. Under distinct circumstances polydispersity seems to have only a minor effect on these measurements.

Two questions arise in connection with the measuring of self-diffusion coefficients of polydisperse polymers with the n.m.r. pulsed field gradient technique: firstly, what is the influence of a polydisperse environment on the diffusion of a polymer molecule, and secondly, in what manner does a distribution of molar masses manifest itself in the averaged measured quantities.

In this paper the effects of polydispersity, which are to be expected in measurements using the n.m.r. pulsed field gradient technique, are discussed and compared with experimental results.

N.M.R. PULSED FIELD GRADIENT TECHNIQUE WITH SAMPLES OF A MOLAR MASS DISTRIBUTION

The quantity measured in the n.m.r. pulsed field gradient technique is the amplitude of the spin echo¹⁰. If the species have a uniform diffusion coefficient D the spin echo amplitude is given by

$$A = A_0 \exp(-(\gamma \delta g)^2 D \Delta) \quad (1)$$

(for symbols see *Figure 1*). A_0 is determined by the nuclear magnetic relaxation with the longitudinal and transverse nuclear relaxation times $T_1(M)$ and $T_2(M)$, respectively, which may be dependent on the molar mass of the polymer molecules. For the stimulated echo (*Figure 1*) we have

$$A_0 = \exp\left(-\frac{2\tau_1}{T_2(M)} - \frac{\tau_2 - \tau_1}{T_1(M)}\right) \quad (2a)$$

and for the primary echo

$$A_0 = \exp\left(-\frac{2\tau}{T_2(M)}\right) \quad (2b)$$

with τ the rf-pulse separation. Usually the pulse sequences are chosen such that $\Delta = \tau_2$ (stimulated echo) or $\Delta = \tau$

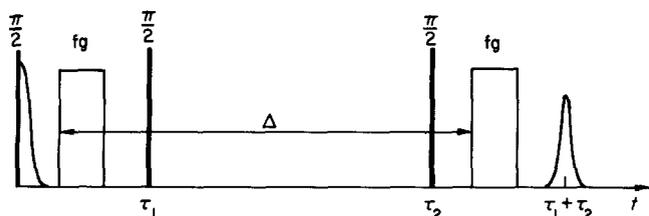


Figure 1 Pulse program for the stimulated echo. After the three $\pi/2$ -rf-pulses at the times 0, τ_1 and τ_2 the spin echo arises at $\tau_1 + \tau_2$. The field gradient pulses fg of magnitude g and duration δ are separated by the diffusion time Δ ($\delta \ll \Delta$). Between τ_1 and τ_2 longitudinal nuclear magnetic relaxation takes place

(primary echo), therefore A_0 is a function of the diffusion time and D is determined by measuring the relative echo amplitude $\psi = A/A_0$ for fixed τ_1 , τ_2 and Δ being dependent on δ or g . The echo attenuation plot $\ln \psi$ vs. $(\gamma\delta g)^2 \Delta$ is a straight line which follows from equation (1)

$$\ln \psi = -(\gamma\delta g)^2 D \Delta \quad (3)$$

If the sample is polydisperse and therefore a distribution of diffusion coefficients exists, ψ turns out to be a superposition of exponentials in the form of equation (1):

$$\psi = \int_0^\infty A_0(M) w(M) \exp(-(\gamma\delta g)^2 D(M) \Delta) dM / \int_0^\infty A_0(M) w(M) dM \quad (4)$$

The molecules of molar mass M contribute to the spin echo with their mass fraction $w(M)$, the contributions are additionally weighted with the factor $A_0(M)$ which in polymer melts also depends on M since there T_1 and especially T_2 values are strongly dependent on the molar mass¹¹ whereas in polymer solutions, except for low molar masses, the nuclear relaxation times are almost independent of the molar mass¹².

The integral in equation (4) was numerically calculated with $A_0 = \text{constant}$. For $w(M)$ we used a log-normal distribution

$$w(M) dM = \frac{1}{(2\pi \ln \bar{M}_w / \bar{M}_n)^{1/2}} \exp\left(-\frac{(\ln M - \ln \sqrt{\bar{M}_w / \bar{M}_n})^2}{2 \ln \bar{M}_w / \bar{M}_n}\right) \times \frac{dM}{M} \quad (5)$$

This is a good approximation for anionically polymerized polystyrene and also for the radically polymerized polystyrene (cf. Figure 2) and the fractions of polyethylene measured by us⁴. For the self-diffusion coefficient $D(M)$ we set

$$D = K \cdot M^{-\alpha} \quad (6)$$

The exponent α is dependent on the concentration regime, where α increases from about 0.6 for infinite dilution up to 2.0 for concentrations greater than the overlap concentration c^* .

The echo attenuation (equation (4)) is only dependent on the polydispersity $P = \bar{M}_w / \bar{M}_n$, one averaged molar mass such as e.g. \bar{M}_w and the exponent α in equation (6).

$$\psi(B) = \frac{1}{(2\pi \ln P)^{1/2}} \int_{-\infty}^{+\infty} \exp\left(-\frac{(\ln m + 0.5 \ln P)^2}{2 \ln P} - B \cdot m^{-\alpha}\right) d \ln m \quad (7)$$

B is equal to $(\gamma\delta g)^2 K \cdot \bar{M}_w^{-\alpha} \Delta$, the echo damping term for an exactly monodisperse polymer with molar mass $M = \bar{M}_w$ of the distribution, $m = M / \bar{M}_w$ is a normalized molar mass.

The integral of equation (7) was calculated with the exponents $\alpha = 0.6$ (dilute solution) and $\alpha = 2.0$ ($c > c^*$, melt) and polydispersities $P = 1.06$ (typical for polystyrene standards), $P = 2.0$ (radically polymerized polystyrene) and $P = 10$ (typical for commercial polyethylene). B was varied up to 3 corresponding to an echo attenuation of a monodisperse sample up to 0.05. The calculated echo attenuation plots are shown in Figure 3. They are already markedly nonexponential for the lowest polydispersity of 1.06.

Equation (4) only holds if the self-diffusion coefficients of the polymer molecules are independent of the length of the neighbouring chains, i.e. if a polydisperse environment does not change the diffusion coefficient. This behaviour is proposed by the reptation concept¹⁴, and due to the observed -2 exponent of the power law on molar mass (equation (6)) reptation is assumed to be the dominant type of motion in polymer melts and solutions with concentrations greater than the overlap concentration c^* or molar masses greater than the critical molar mass M^* of overlapping ($c^* \simeq M^* / N_a R_G^3(M^*)$ with N_a the Avogadro constant and $R_G(M^*)$ the radius of gyration). Therefore equation (4) can be expected to be fulfilled for concentrations greater than the overlap concentration c^* .

When, for solutions of polydisperse samples, the concentration is lowered, one reaches a concentration c^* at which the molecules with the smallest molar mass become

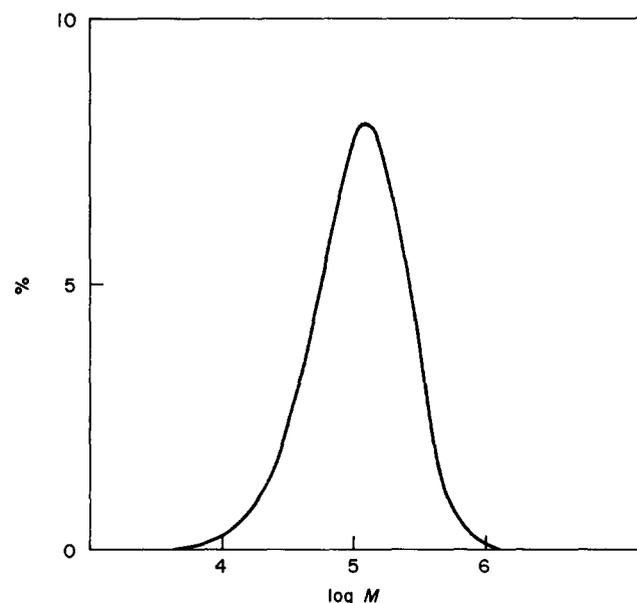


Figure 2 Molar mass distribution of the radically polymerized polystyrene. $\bar{M}_w = 145\,000$ and $\bar{M}_w / \bar{M}_n = 2.0$ (determined by g.p.c.)

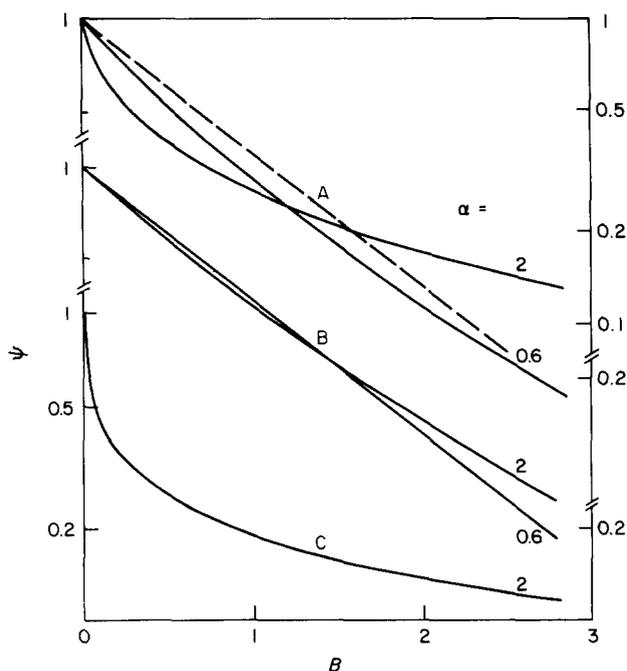


Figure 3 Calculated echo attenuation plots $\lg \psi$ vs. B for a log-normal distribution of molar masses with polydispersities $\bar{M}_w/\bar{M}_n=2$ (A), $=1.06$ (B) and $=10$ (C) and for the exponent α in equation (6) $=0.6$ and $=2$. An exact monodisperse polymer with a molar mass equal to \bar{M}_w of the distribution gives the broken line. B is equal to $(\gamma\delta g)^2 D(\bar{M}_w)\Delta$

non-overlapped. Then longer overlapping molecules are dissolved in a mixture of the solvent and the smaller non-overlapping molecules. We have two different diffusion mechanisms for the smaller and the larger molecules and equation (4) will not then be fulfilled. For non-overlapping solutions, in the dilute regime, the concentration dependence of the self-diffusion coefficient can be written in the form of

$$D = D_0(1 - k_d c/c^*) \quad (8)$$

where c/c^* is the hydrodynamic volume fraction of the polymer coils in the dilute solution and k_d is a constant¹⁵. For a polydisperse sample with concentration c the second term is the same for all the molar masses of the distribution, and the self-diffusion coefficient of the different molar masses should vary similarly to D_0 for infinite dilution, i.e. with $M^{-0.6}$. Equation (4) should hold with exponent α being about 0.6.

As will be seen later, a polydisperse sample can show an exponential echo attenuation within experimental error and a self-diffusion coefficient can be determined with equation (3). Clearly equation (4) does not hold in these cases. An averaging process causes the same echo attenuation for all molar masses. Neglecting this averaging one can write, for the measured self-diffusion coefficient,

$$D_w = \int_0^\infty w(M) \cdot K \cdot M^{-\alpha} dM \quad (9)$$

$$\equiv K \cdot \bar{M}_D^{-\alpha} \quad (10)$$

which is related to a 'diffusion-average' of the molar mass

\bar{M}_D utilised in equation (6) experimentally. For \bar{M}_D we obtain

$$\bar{M}_D = \left(\int_0^\infty w(M) M^{-\alpha} dM \right)^{-1/\alpha} \quad (11)$$

It is simple to show that

$$\bar{M}_D(\text{conc.}) < \bar{M}_n < \bar{M}_D(\text{dilute}) < \bar{M}_w \quad (12)$$

where $\bar{M}_D(\text{conc.})$ and $\bar{M}_D(\text{dilute})$ pertain to the overlapping concentration regime ($\alpha=2$) and to the dilute regime ($\alpha=0.6$), respectively, and also that the ratio \bar{M}_D/\bar{M}_w is only dependent on the polydispersity and on the concentration regime (the α value which applies). Therefore, a plot of $\log D$ vs. $\log \bar{M}_w$ should give a correct α value in equation (6) if the samples have constant polydispersities⁸. However, if one observes a single exponential echo attenuation, equation (9) is only a fair approximation because it neglects the precise nature of the averaging process and the conclusions drawn from equation (9) deserve a more detailed investigation.

If equation (4) is satisfied, which is yet to be proved experimentally, the diffusion coefficient of the weight averaged molar mass $D(\bar{M}_w)$ can be evaluated from the non-exponential echo attenuation plot by fitting the experimental data to the calculated curves (cf. Figure 3) via the parameter B . For this to occur the molar mass distribution, the exponent α and the molar mass dependences of the nuclear magnetic relaxation times must be known.

EXPERIMENTAL

The measurements were carried out as previously described² using the stimulated echo method (cf. Figure 1). In this case the magnetization relaxes between τ_1 and $\tau_2 - \tau_1$ with T_1 which, in polymer systems, is much greater than T_2 . Therefore the time τ_2 can be deliberately chosen as being considerably long and the cross-term proportional to $g \cdot g_0$ (g_0 is the small steady gradient) is much smaller than with the primary echo¹⁶ and can therefore be neglected. The spectrometer response is linear up to echo attenuations of at least 0.1 which was tested with a glycerol sample (cf. Figure 5).

We measured samples of a radically polymerized polystyrene with known molar mass distribution (cf. Figure 2) dissolved in toluene-d8 and mixtures of polystyrene standards (1:1 by weight) dissolved in benzene-d6 at room temperature. The sample data are given in Table 1. A commercial low-density polyethylene with a polydispersity of about 10 and a \bar{M}_w of about 2×10^5 and an approximately log-normal molar mass distribution determined by g.p.c. was measured at a temperature of 190°C.

The self-diffusion coefficients in the solutions were evaluated on the assumption of molar mass independent nuclear relaxation times, i.e. A_0 being constant. If the echo attenuation of a mixture of two polystyrene standards was non-exponential we decomposed it into two single exponentials with equal intensity. This decomposition could be achieved if the decay constants of the exponentials differed by more than a factor of two to three and

experimental errors of the data points were as small as in the typical echo attenuation plots shown in Figures 4 and 5.

RESULTS AND DISCUSSION

In Figure 4 the echo attenuation plots of three samples of the radically polymerized polystyrene are shown. In contrast to the calculated curves (Figure 3) the plots are obviously linear within experimental error, except for the

highest concentration, and one averaged diffusion coefficient can therefore be determined. The mixtures of the polystyrene standards show exponential as well as non-exponential echo attenuations depending on the polydispersity of the mixture and the concentration. Two typical plots are shown in Figure 5, and all the results are given in Table 1. Included in this Table are the \bar{M}_w/\bar{M}_n values of the mixtures, the concentrations given as volume fractions of the polymer ϕ_2 and those divided by the overlap concentration as c/c^* , and the measured self-

Table 1 Sample characteristics

Sample	Molar masses of the components		\bar{M}_w/\bar{M}_n	Volume fraction of the polymer ϕ_2	c/c^{*a}	Critical molar mass of overlapping ^b M^*	Measured self-diffusion coefficients		Self-diffusion coefficients of the pure components ^c	
	M_1	M_2					D_1	D_2 (ms s ⁻¹)	D_1^p	D_2^p (ms s ⁻¹)
Ia	19 000	12 000	1.05	0.079	0.375	85 000	8.7×10^{-11}	6.6×10^{-11}	9×10^{-11}	
Ib	19 000	12 000	1.05	0.366	1.6	14 500	3.5×10^{-12}	3.8×10^{-12}	7.5×10^{-12}	
IIa	110 000	12 000	2.8	0.06	0.63	115 000	2.3×10^{-11}	8×10^{-11}	2.4×10^{-11}	
IIIa	110 000	19 000	2.0	0.037	0.41	200 000	4×10^{-11}	8×10^{-11}	3.2×10^{-11}	
IIIb	110 000	19 000	2.0	0.325	3.5	165 000	6.0×10^{-13}	2.7×10^{-12}	3.5×10^{-13}	
IVa	470 000	110 000	1.6	0.045	1.3	160 000	4.8×10^{-12}	2.6×10^{-11}	2.0×10^{-12}	
IVb	470 000	110 000	1.6	0.083	2.4	80 000	1.7×10^{-12}	7.0×10^{-12}	6.0×10^{-13}	
Va	470 000	250 000	1.1	0.046	1.6	160 000	4.4×10^{-12}	2.0×10^{-12}	5.5×10^{-12}	
Vb	470 000	250 000	1.1	0.08	2.7	83 000	1.4×10^{-12}	7×10^{-13}	2.0×10^{-12}	
PS25	$\bar{M}_w = 145 000$		2.0	0.011		850 000	5.5×10^{-11}			
PS19				0.046		160 000	2.6×10^{-11}			
PS11				0.20		29 000	2.5×10^{-12}			
PS9				0.36		15 000	9×10^{-14d}			

^a Calculated with $c^* = 2/N_a(V_1^H/M_1 + V_2^H/M_2)$ with the hydrodynamic volumes V_i^H determined after ref. 27

^b Determined from the experimental values of ref. 2

^c For $c/c^* < 1$ in solutions of the same c/c^* , for $c/c^* > 1$ in solutions of the same ϕ_2

^d $D(\bar{M}_w)$

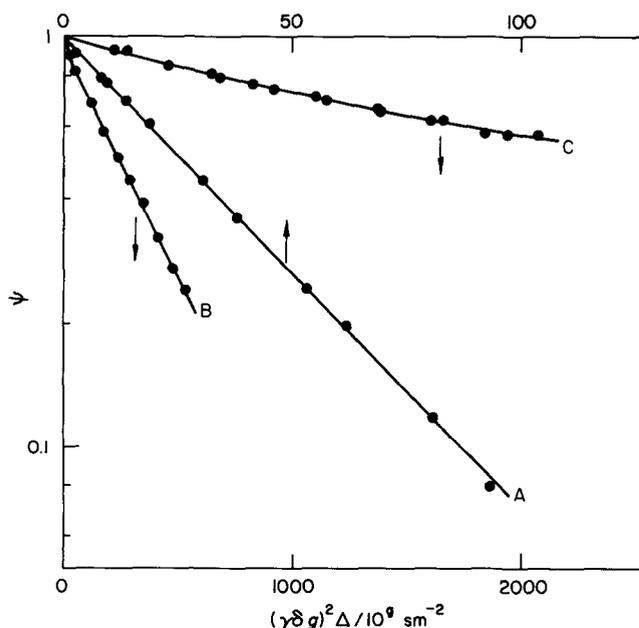


Figure 4 Echo attenuation plots for the radically polymerized polystyrene dissolved in toluene-d₈ with concentrations of 4.6% (A), 20% (B) and 36% (C). The experimental error is approximately equal to the symbol size

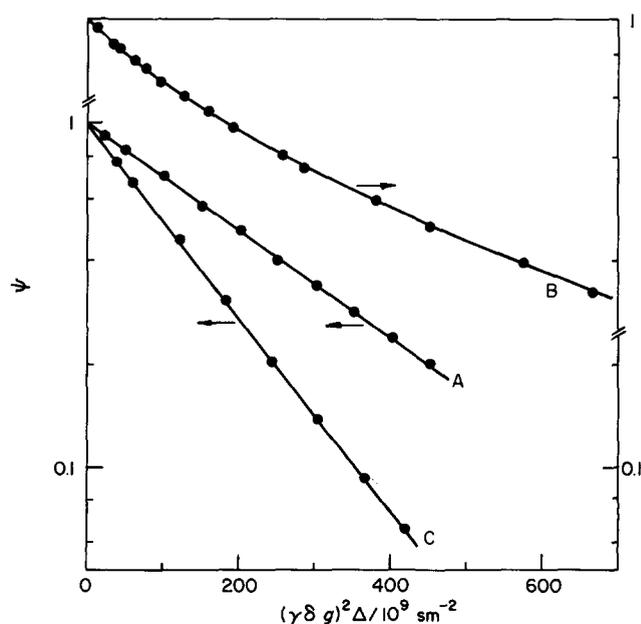


Figure 5 Echo attenuation plots for the mixtures Ib (A) and IVb (B) of polystyrene standards dissolved in benzene-d₆. The echo attenuation of a glycerol sample (C) is shown for comparison

diffusion coefficients of the mixture (one for exponential echo attenuation plots and two for non-exponential plots). In the last column are given the self-diffusion coefficients of each of the components in a pure solution of the same c/c^* as in the mixture (for nonoverlapping solutions, $c/c^* < 1$) or of the same ϕ_2 as in the mixture (for overlapping solutions, $c/c^* > 1$) according to ref. 2. In the sixth column the critical molar mass of overlapping M^* is given.

The overlapping concentration regime is represented by the samples IIIb, IVb, Va, Vb and PS9. The molar masses of the smaller components of the mixtures are only slightly greater than M^* , at most by a factor of three. All molar masses including the number average of the polystyrene of sample PS9 are smaller than the critical molar mass of entanglements $M_e = M_c/\phi_2^{17}$ with $M_c = 38\,000$. We can observe a decrease in the self-diffusion coefficient of the smaller component and an increase in the self-diffusion coefficient of the larger component by a factor of two to three in comparison with the self-diffusion coefficients of the pure polymers in a solution of the same concentration. The samples Va and Vb then show a single exponential echo attenuation. This behaviour is in contradiction to the reptation concept, the self-diffusion coefficient of a chain depends on the chain length of the neighbouring chains, though for solutions of monodisperse polystyrenes in this concentration regime the dependence $D \sim M^{-2}$ proposed by the reptation concept is valid^{2,3}. A similar effect was observed by Leger *et al.*¹⁸ who measured the diffusion of labelled chains mixed with unlabelled chains in solution using the forced Rayleigh scattering technique. The self-diffusion coefficients of the labelled chains decrease with increasing matrix chain length (at constant total concentration). For the sample PS9 with a M^* much smaller than M_n , equation (4) is found to be approximately fulfilled, the chains behave nearly independently of the polydisperse surrounding chains. By comparison of the measured with the calculated echo attenuation plot, $D(M_w) = 9 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ is obtained. This value agrees very well with the self-diffusion coefficient for the molar mass of 145 000 (the M_w of sample PS9) at this concentration determined in a previous investigation².

The non-overlapping regime is represented by samples Ia, IIa, IIIa and PS25. We observe also a slight averaging which was explained earlier in this paper. The diffusion process in the mixture seems to be slightly speeded up in comparison with the diffusion process in the pure components. The sample PS25 has a self-diffusion coefficient of a monodisperse polystyrene (molar mass of about 70 000) which is less than the M_D calculated using equation (11).

The samples Ib, IVa, PS11 and PS19 belong to the concentration region between $c^{*'} and c^* where the larger macromolecules overlap and the smaller molecules do not. Here we also observe an averaging of the diffusion coefficients in the mixture. For small molar masses (sample Ib) the diffusion in the mixture is slowed down and for higher molar masses (sample IVa) the diffusion is slightly speeded up.$

The averaging process clearly depends on the concentration regime where, for very high dilution it must vanish since the hydrodynamic interaction between the polymer molecules disappears. Von Meerwall observed a non-exponential echo attenuation in a polydisperse sa-

mple of a poly(methacrylate) for $c \ll c^*$ which obeys an equation in the form of equation (4)⁷. Coming to very high concentrations and to the melt, the diffusion of a chain should be independent of the matrix chain length (apart of free volume effects) as suggested by the reptation model¹⁴. This has been confirmed experimentally for molar masses greater than the critical molar mass of entanglements $M_c^{6,19,20}$, but not for molar masses smaller than $M_c^{20,21}$ although the relation $D \sim M^{-2}$ is observed down to molar masses much smaller than M_c . Our results for polymer solutions support the assumption that in non-entangled solutions the tube is not fixed though $D \sim M^{-2}$ holds.

In polymer melts the molar mass dependent factor $A_0(M)$ must also be taken into account. It is a decreasing function of M , and the decrease becomes greater for longer diffusion times. The observed echo attenuations are still less exponential than calculated with a constant $A_0(M)$. This can be clearly seen in Figure 6 where the echo attenuation of a commercial low-density polyethylene with a broad molar mass distribution is shown. The plot is extremely non-exponential, and no self-diffusion coefficient can be determined. The upper curve is calculated using equation (4) and $A_0(M)$ being constant, it can be seen that only the first part of the echo attenuation (cf. Figure 3) is measured with a strong weighting of the lower molar masses due to the longer nuclear relaxation times. The factor $A_0(M)$ is now important where it decreases with increasing molar mass, and this decrease becomes more pronounced for longer diffusion times. Therefore for long diffusion times the lower molar masses become still more weighted than for shorter diffusion times resulting in a faster decay of the echo attenuation for longer diffusion times which can be seen in Figure 6. The self-diffusion coefficients seem to increase with increasing diffusion time. However, this is only an effect of molar mass dependent nuclear relaxation times and polydispersity. Skirda *et al.*²² have observed a similar increasing decay of the echo attenuation with increasing diffusion time measuring the self-diffusion of poly(ethylene glycol) with a polydispersity of 1.2 in the melt. This should also be caused by the effects discussed above rather than by an effect of chemical exchange as discussed by those authors.

In the published n.m.r. self-diffusion data of polymers in the melt (e.g. refs. 4 and 5) the polydispersity of the

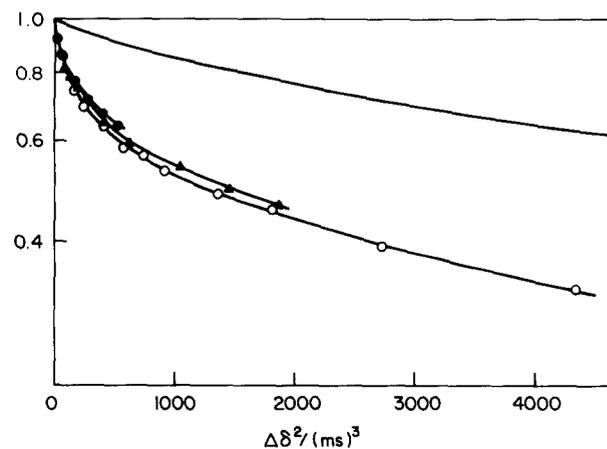


Figure 6 Echo attenuation of a commercial low-density polyethylene ($M_w \approx 2 \times 10^5$, $M_w/M_n \approx 10$) at 190°C measured by the stimulated echo method with $\tau_1 = 8$ ms. The diffusion times are 58 ms (●), 208 ms (△) and 908 ms (○). The echo attenuation calculated with equation (4) and $A_0(M) = \text{constant}$ is shown by the upper curve indicating that in the experimental curves the low molar masses are strongly weighted

samples was not taken into account or at least not appropriately. A re-evaluation of the experimental data of ref. 4, considering the polydispersity of the samples and the effect of $A_0(M)$, results in lower self-diffusion coefficients²³. These values agree well with those obtained by other methods²⁴.

Lastly it should be mentioned that Chalych *et al.*²⁵ have observed that in measurements of mutual diffusion in polymer solutions by means of concentration-distance curves, a polydisperse sample behaves much like a monodisperse sample and a similar averaging is also observed for low molecular weight compounds where the distribution of self-diffusion coefficients of a mixture of solvents is considerably smaller than the distribution of the self-diffusion coefficients of the corresponding pure solvents²⁶.

CONCLUSIONS

Due to the strong dependence of the self-diffusion coefficient on the molar mass, the echo attenuation plot of the spin echo in the n.m.r. pulsed field gradient technique should be non-exponential if a molar mass distribution of the sample exists. This should be seen for polydispersities as low as 1.06 which are common for commercially available polystyrene standards. However, the experiments show that in solutions, depending on the concentration regime, an averaging in the diffusion process is present leading to a considerably smaller distribution of self-diffusion coefficients than calculated. This is not in accordance with the assumption of a fixed tube which is made within the reptation concept.

For very dilute and concentrated solutions and entangled melts the averaging vanishes, the macromolecules diffuse independently of the polydisperse environment and the echo attenuation plot is simply the sum of the contributions of each molar mass of the distribution. In the melt the echo attenuation plot is additionally influenced by the molar mass dependent nuclear relaxation times resulting in a considerable non-exponential and

diffusion-time-dependent echo attenuation. This should not be misinterpreted as a time-dependence of self-diffusion coefficients.

ACKNOWLEDGEMENTS

The author would like to thank Drs D. Geschke, J. Kärger and E. Straube for their advice and stimulating discussions and Dr E. Brauer for the g.p.c. measurements.

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